Low-Cost Adsorbents from Agricultural By-Products Impregnated with Phosphoric Acid

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Abstract

Agricultural and forestry residues, or general biomass, are considered as suitable raw materials for the production of low-cost adsorbents. In this work, activated carbon was prepared by activation of agricultural by-products in the presence of phosphoric acid. Different agricultural residues such as bagasse, apricot stones, almond, hazelnut, pistachio and walnut hard shells are used as precursors. Different preparation parameters like the activating reagent/precursor ratio, final activation temperature and activation time were examined to evaluate the influence of the activation conditions on both the yield and quality of the obtained activated carbon. The results indicated that the selection of final activation temperature, activation time and activating ratio was important in the quality of activated carbon. The surface area and ash content of the produced activated carbon were compared with those of commercial ones. Based on the results from a variety of raw materials, it has been found that activated carbon from hard shells of apricot stones had the best adsorption properties and the largest surface area. This activated carbon could be used in the recovery of precious metal ions such as gold and silver from wastewaters.

Keywords

Adsorbent; Activated Carbon; Chemical Treatment; Agricultural By-Products; Phosphoric Acid

Introduction

Nowadays, activated carbons due to their structural properties and relatively low cost are among the more industrial adsorbents. They are widely used for the separation and storage of gases, the recovery of solvents, the removal of organic pollutants from drinking water, the recovery of metal ions from waste waters (Bansal and Goyal, 2005; Caglayan and Aksoylu, 2013; Cox *et al.*, 2005; Patric, 1995; Marsh and Rodriguez-Reinoso, 2006) and as catalysts or catalyst support (Rubio Gomez *et al.*, 1999; Aksoylu *et al.*, 2001, 2003; Nickolov *et al.*, 2013). As environmental pollution has been becoming a very serious problem, the need for the utilization of activated carbon is increasing.

Physicochemical characteristics of activated carbon depend mainly on the kind of raw material used and the activation process. These properties may not relate directly to their effectiveness in the applications of activated carbon, but they are important for commercial utilization (Bansal and Goyal, 2005; Marsh and Rodriguez-Reinoso, 2006; Toles *et al.*, 2000; Ahmenda *et al.*, 2000).

The production process of activated carbon is mainly divided into three steps: dehydration, carbonization, and activation. Dehydration is a drying process of the moisture removal from the raw material, and during carbonization organic matter contained in the raw material changes into primary carbon, which is a mixture of amorphous and crystallized carbon, tar, and ash. Activation, the main step in the process, is generally carried out in two ways, gas activation and chemical activation. Gas activation is a physical process in which raw material passes through carbonization at a low temperature and is usually activated by CO_2, water steam, and air. The most widely used type of gas activating process is the one utilizing steam as the activating gas under high temperatures (800–1000°C) and long treatment conditions. The disadvantage of the gas activation process lies in the low yield and the lack of homogeneity of the product (Bansal and Goyal, 2005; Gonzalez *et al.*, 2009).

In contrast, chemical activation utilizes chemicals, such as $ZnCl_2$, H_3PO_4, H_2SO_4, KOH, and $CaCl_2$ that have dehydration and oxidation characteristics influencing pyrolytic decomposition and inhibiting formation of tar, thus enhancing the yield of activated carbon. Carbonization and activation are usually carried out simultaneously in the chemical activation process (Marsh and Rodriguez-Reinoso, 2006; Arjmand *et al.*, 2006).

Different chemical agents, known for a long time, can

be used in the chemical activation process, and out of all of them, phosphoric acid and zinc chloride are commonly used as activation reagents. The chemical activation process is known to be effective for the production of activated carbon used for water/wastewater treatment. There have been several studies regarding the change in adsorbent capacity and specific surface area based on the kind of chemicals and activating conditions (Benaddi *et al.*, 2000; Diaz–Teran *et al.*, 2003; Gonzalez-Serano *et al.*, 1997; Hayashi *et al.*, 2000; Kim *et al.*, 2001; Molina–Sabio *et al.*, 1996; Moreno Castillia *et al.*, 2001; Olivares-Marín *et al.*, 2012).

There are many precursors from which activated carbons can be obtained. Raw materials for activated carbon are chosen depending on their purity, price, potential extent of activation, and stability of supply. Presently, the most commercial activated carbons are prepared from coal/lignite (42%) and wood/coconut (45%) (Patric, 1995). A large volume of agricultural by-products is lignocellulosic wastes that may offer inexpensive and renewable sources of activated carbon. This option is particularly attractive since the yearly harvested and processed various agricultural crops in Iran yields considerable quantities of agricultural by-products. Moreover, by choosing a suitable starting material, the use may reduce solid waste pollution, while reducing the cost of raw materials for the production of activated carbon. The common examples of these wastes are fruit stones (apricot, peach, and cherry stones), nutshells (almond, walnut, and pecan), rice hulls, bagasse, grape seeds, olive waste, corncob, etc. (Hayashi *et al.*, 2002a, 2002b; Johns *et al.*, 1998; Lafi, 2001; Gergova and Eser, 1996; Bansode *et al.*, 2003; Genceli *et al.*, 2002; Savova *et al.*, 2001; Toles *et al.*, 1997; Olivares-Marín *et al.*, 2012; Tongpoothorn *et al.*, 2011; Yang and Lua, 2003;).

In Iran, activated carbon required for industries such as oil and gas, food, pharmaceutical, water and wastewater treatment, gold recovery has been imported from other countries. There is an opportunity here to reduce the cost of these processes by producing activated carbon in Iran using domestic raw material resources (Fouladi Tajar *et al.*, 2009; Kaghazchi *et al.*, 2010, Soleimani and Kaghazchi, 2005, 2008 a,b). Residues from agriculture and food industries are the non-product outputs produced from the growing and processing of raw agricultural materials such as almond, apricot or pistachio hard shells, rice husk and olive wastes. In Iran, these low–value biomass is used inefficiently as a fuel, otherwise discharged as wastes.

All of the materials are renewable on the yearly basis, unlike coal, peat wood. Since Iran is among top four countries in the world for these products, the idea of the production of activated carbon from these by-products is economically justified (Soleimani and Kaghazchi, 2004, 2008a,b; Arjmand *et al.*, 2006).

In the present work, we have attracted more attention to the effective use of domestic agricultural by-products being widely distributed in Iran in order to solve the lack of coconut shells. We performed chemical activation of these materials such as bagasse, hard shells of apricot stones, almond, walnut and hazelnut for preparation of activated carbon.

Experimental

Raw Materials

Six kinds of agricultural by-products including bagasse, apricot stones, almond, hazelnut, pistachio and walnut hard shells were used as the raw materials of activated carbons. These wastes were selected because of their availability and desirable physical characteristics as a precursor.

An Elemental analysis of raw materials was performed by using a CHNS-O (series 2400II Perkin Elmer, Inc.) elemental micro analyzer. In order to assess the effect of the compositions of the raw materials on the properties of activated carbons, the content of lignin, cellulose, extractable materials and ash content were determined according to TAPPI standards (1988a, 1988b, 1993). The content of lignin and cellulose may be one of the criteria for the selection of appropriate raw materials in accordance with the requirements for the properties of the activated carbon (Madadi Yeganeh *et al.*, 2006).

Results of elemental analysis and the chemical composition of these agricultural wastes have been indicated in **Table 1**. Because of low ash content, these raw materials have potential to be used as feedstock for activated carbon production. Bagasse has a high ash content whereas hard shells of apricot stones have a relatively low ash content. High ash content in starting material is undesirable because it reduces the mechanical strength and adsorption capacity of activated carbon. The cellulose content is highest in bagasse and lowest in walnut shells. The elemental analysis data indicated that the raw materials have a variation in the composition. Hazelnut shells have the highest C content. Bagasse, on the other hand, has the lowest C and H contents. Apricot stones and almond shells have rather similar elemental compositions.

TABLE 1 CHEMICAL COMPOSITION OF THE RAW MATERIALS FOR ACTIVATED CARBON PREPARATION

Raw materials	C [wt%]	H [wt%]	Ash[wt%]	Cellulose[wt%]	Lignin [wt%]	Extractable materials [%]
Almond shell	50.30	6.05	1.54	39.25	27.00	0.47
Apricot stone	50.50	6.03	0.20	39.75	34.50	0.41
Bagasse	46.00	6.00	3.40	42.80	15.80	
Hazelnut shell	51.90	5.91	1.20	40.5	27.2	6.2
Pistachio shell	47.30	5.76	1.26	42.00	13.5	0.18
Walnut shell	49.00	5.75	1.70	34.50	33.30	1.16

Activated Carbon Preparation

Activated carbon prepared from agricultural by-products by a chemical activation process in seven stages (Soleimani and Kaghazchi, 2007):

1. Agricultural by-products were crushed and sieved to obtain desired size fractions (0.5–1.2 mm) using a conventional sieve-shaker,

2. The selected fraction of particle size was dried in an air oven at 100°C for over night,

3. The dry precursors were impregnated with phosphoric acid solution at 25°C,

4. The mixture was kept in an air oven at 100°C for over night,

5. The impregnated precursor was subjected to carbonization and an activation process in a programmable electrical furnace (Nabertherm Labothrem),

6. The activated product was washed extensively with hot distilled water to remove free acid,

7. The washed activated carbon was dried overnight in an air oven at 100°C.

The influence of main preparation parameters (activation temperature, activation time, and activating reagent/precursor ratio) on both yield and quality of the prepared carbon were investigated.

High yields are desirable in activated carbon production and help reduce the production cost. The yield of activated carbon is calculated as:

$$Carbon\ yield[\%]=\frac{Activated\ carbon\ weight}{Raw\ material\ weight}*100 \qquad (1)$$

The reagent recovery ratio indicates how much of the impregnated reagent could be recovered after one cycle of the process. The percent of H_3PO_4 recovery ratio is determined by Eq. (2):

$$Reagent\ recovery = \frac{Weight\ of\ product\ before\ washing\text{-}\ weight\ of\ end\ product}{H_3PO_4\ weight\ for\ impregnation}*100 \qquad (2)$$

Characterization of the Prepared Activated Carbon

To characterize the activated carbons produced, its iodine number, specific surface area and ash content was determined.

Iodine number [mg I_2/ g Carbon] indicated the extent of micro pore distribution in the carbon and was measured by titration at 30°C based on the standard method (ASTM standard, 2000a). This parameter was used to evaluate the activated carbon adsorption capacity. The activated carbons were ground until 95 wt% or more will pass through a 325-mesh screen. From each sample, three small batches of dried activated carbons (0.1 g) were taken and fully wetted with 10 ml of 5 wt% HCl. Then 100 ml of 0.025 M standard iodine solution was poured into the flask, and the contents were vigorously shaken for 30 s. After quick filtration, 50 ml of the solutions were titrated with standard sodium thiosulfate with starch as an indicator. The concentration of iodine in the solution was thus calculated from the total volume of sodium thiosulfate used.

The specific surface area of activated carbons was measured by the BET (Brunaeur –Emmet–Teller) method using the adsorption–desorption isotherm of N_2 at 77 K. A NOVA® 1000 surface area analyzer (Quantachrom Instruments) was used for this parameter by applying the 5-point BET. Before measuring the isotherm, the samples were heated at 473 K for 2 h in vacuum for degassing the surface (Brunauer et al., 1938).

Apparent or bulk density is a measure of the weight of material that can be contained in a given volume under specified conditions. To measure bulk density, a 10 mL cylinder was filled to a specified volume with dried adsorbent. The cylinder was weighed. The bulk density was then calculated as (ASTM Designation: D 2854-96., 2000b):

$$Bulk\ density = weight\ of\ dry\ material\ [g]/ volume\ of\ packed\ dry\ material\ [ml] \qquad (3)$$

The Ash content (ash%) of an activated carbon is the residue that remains when the carbonaceous portion is

burned off. Ash content of activated carbon was determined by standard methods (ASTM standard, 2000c). Approximately 1–2 g of powdered activated carbon was placed into weighed ceramic crucibles. Activated carbon and crucibles were dried at 80°C for 24 h and reweighed to obtain the dry carbon weight. The samples were heated in an electrical furnace at 650 ± 25°C for 3 h. The crucibles were cooled in a desiccator, and remaining solids (ash) were weighed. The percent of ash was calculated by:

$$\text{Ash \%} = [\text{remaining solids weight [g]}/ \text{original carbon weight [g]]}*100 \quad (4)$$

To ensure the accuracy and reproducibility of collected data, experiments and analysis were carried out in duplicate and the mean value of two data set was presented.

Finally, a comparison was made for the gold separation capacities of produced activated carbon and commercial activated carbons.

Results and Discussion

Influence of Final Activation Temperature

Table 2 indicate the influence of final activation temperature on the production of activated carbon from different agricultural by-products. For these experiments, the activation time was 1.5 h and activating reagent/precursor ratio (activating reagent/p recursor ratio=Impregnation ratio= H_3PO_4 weight*100/ raw material weight) was about 50%. As seen from **Table 2**, the carbon yield did not change substantially. The highest yield was achieved when apricot stones were activated at 400°C. It can be seen that increasing the activation temperature decreases the carbon yield and iodine number. This result is usually dependent on the kind of the raw material. Activated carbons prepared from hard shells of apricot stones had the highest iodine number and surface area.

Influence of Activation Time

The changes in the iodine number and the yield of activated carbon produced from agricultural by-products have been investigated as a function of activation time. From the data in **Table 3**, it is clear that the activation time has a significant effect on the carbon yield, chemical activation agent recovery and adsorption property. When activation is carried out for a longer time, the iodine number decreases gradually. That is, under extended activation, the micro porous structure of the produced activated carbon deteriorated and turns into macro pores.

Increasing the activation duration from 1 h to 1.5 h, caused the product yield reduction rapidly. This was possibly due to the volatilization of organic matter from precursors, which resulted in the formation of activated carbon.

TABLE 2 INFLUENCE OF FINAL ACTIVATION TEMPERATURE

Raw material	carbon yield [%]	Recovery [%]	Iodine number [mg I_2/g C]	Surface area [m²/g]
Final temperature = 500°C				
Almond shell	24.9	71.2	412.0	169.1
Apricot Stone	30.0	76.2	450.0	251.1
Hazelnut shell	21.4	76.1	440.0	229.5
Walnut shell	29.4	69.4	420.0	186.3
Final temperature = 400°C				
Almond shell	24.8	76.3	464.0	269.4
Apricot Stone	32.6	72.8	490.0	337.5
Hazelnut shell	24.1	81.1	463.0	279.2
Walnut shell	22.2	86.6	424.0	195.0

TABLE 3 INFLUENCE OF ACTIVATION TIME
(Final activation temperature = 500°C, Impregnation ratio = 50%)

Raw material	Carbon yield [%]	Recovery [%]	Iodine number [mg I_2/g C]
Activation time = 1 h			
Almond shell	45.6	67.5	737.0
Apricot Stone	45.8	67.0	836.0
Bagasse	29.1	54.5	656.0
Hazelnut shell	48.2	66.3	731.0
Walnut shell	46.5	68.2	679.0
Activation time = 1.5 h			
Almond shell	24.9	71.2	412.0
Apricot Stone	30.0	73.4	450.0
Bagasse	14.8	64.8	387.0
Hazelnut shell	21.4	76.1	440.0
Walnut shell	29.4	69.4	420.0

Influence of Activating Reagent /Precursor Ratio

In chemical activation, it was well demonstrated that the impregnation ratio is one of the main variables having a profound effect on the adsorption properties of activated carbon. The addition of different ratios of phosphoric acid to bagasse, apricot stones, almond, pistachio and walnut hard shells had been studied. The results have been shown in **Figs 1–5**.

The data in **Figs. 1–5**, indicated that the iodine number of prepared activated carbon was substantially influenced by the phosphoric acid concentration in the impregnating solution, whereas the carbon yield did not vary much. According to these data, the iodine number of activated carbon from bagasse has increased from 365 to 790 mg I_2/g C with an increase of impregnation ratio from 10 to 100%, and the iodine number of activated carbon from hard shells of apricot stones has increased from 121 to 1082 mg I_2/g C with an impregnation ratio increasing from 0 to 85%.
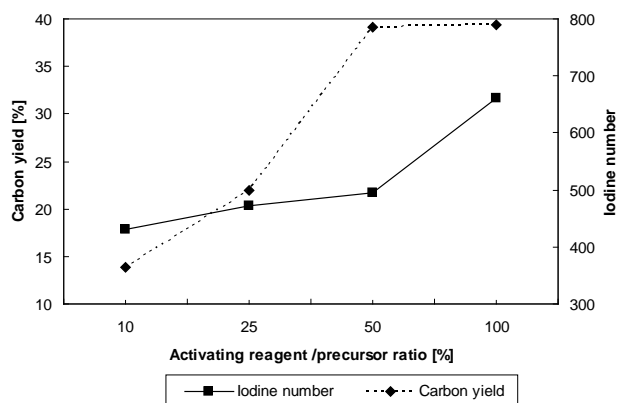
FIG. 1 INFLUENCE OF ACTIVATING REAGENT /PRECURSOR RATIO FOR ACTIVATED CARBON PREPARED FROM BAGASSE: FINAL ACTIVATION TEMPERATURE: 500°C; ACTIVATION TIME: 1h
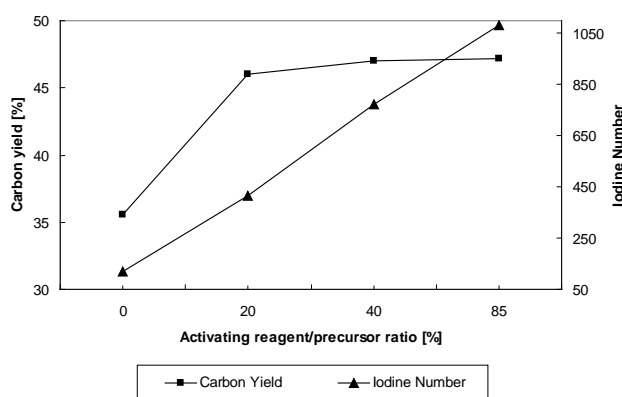

FIG.2 INFLUENCE OF ACTIVATING REAGENT /PRECURSOR RATIO FOR ACTIVATED CARBON PREPARED FROM HARD SHELLS OF APRICOT STONES: FINAL ACTIVATION TEMPERATURE: 400°C; ACTIVATION TIME: 2h
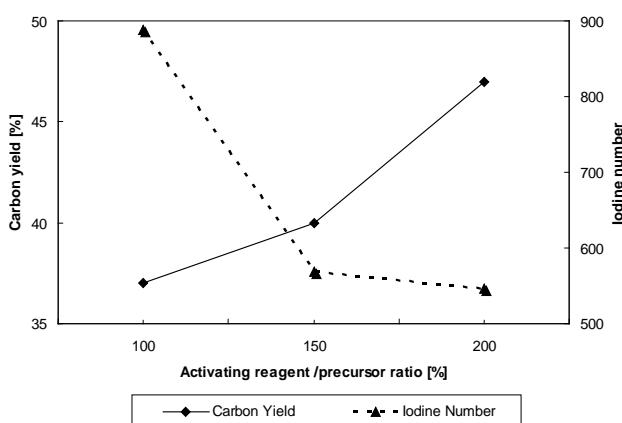

FIG.3 INFLUENCE OF ACTIVATING REAGENT /PRECURSOR RATIO FOR ACTIVATED CARBON PREPARED FROM ALMOND SHELLS: FINAL ACTIVATION TEMPERATURE: 400°C; ACTIVATION TIME: 1h

In the cases of higher ratios of over 100% (**Figs. 3–5**), the iodine numbers of produced activated carbon decrease rapidly, it may be caused by the deterioration of the micro porous structure of activated carbon due to excessive dehydration (the iodine numbers of activated carbons from almond, pistachio and walnut

shells decreased from 888 to 546, 517 to 413, and 924 to 318 mg I_2/g C, respectively with an increase of impregnation ratio from 100 to 200%.
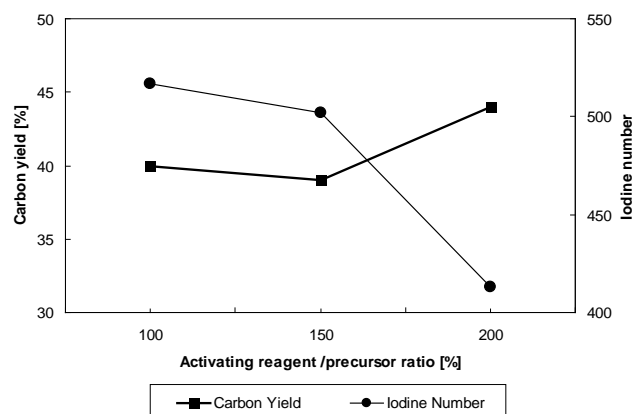

FIG.4 INFLUENCE OF ACTIVATING REAGENT /PRECURSOR RATIO FOR ACTIVATED CARBON PREPARED FROM PISTACHIO SHELLS: FINAL ACTIVATION TEMPERATURE: 400°C; ACTIVATION TIME: 1h
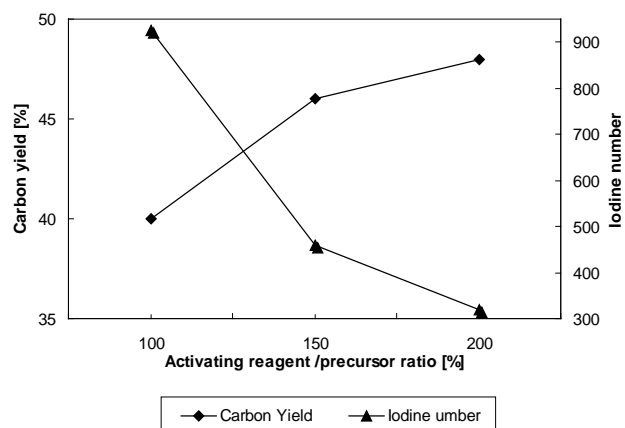

FIG.5 INFLUENCE OF ACTIVATING REAGENT /PRECURSOR RATIO FOR ACTIVATED CARBON PREPARED FROM WALNUT SHELLS: FINAL ACTIVATION TEMPERATURE, 400°C; ACTIVATION TIME: 1h

Comparison of Gold Separation with Different Activated Carbons

The potential of gold separation from aqueous solution with prepared activated carbons from apricot stones (HSAS C) and pistachio hard shell (HSP C) was compared with three types of imported industrial activated carbon. These commercial activated carbons are:

- Mooteh C: activated carbon has been applied in Mooteh mine for gold recovery process in Iran

- Gas C: activated carbon has been applied in gas phase separation

- CECA C: activated carbon from CECA company

HSAS C and HSP C samples have been prepared at

the following operating conditions:

Impregnation ratio is 50%, final activation temperature is 400°C, activation time is 1h, particle size is 1.2–1.7 mm (Soleimani, 2007).

The details of gold adsorption can be found elsewhere (Soleimani and Kaghazchi, 2008a,b). In summary, a measured volume of gold solution (50 m*l*) was contacted with a given weight of activated carbon in glass bottles. Samples were shaken at room temperature for 6 h. In all experiments the pH of solutions was kept constant at 10.5. The properties of these activated carbons and the percentage of gold separation are listed in **Table 4**.

TABLE 4 COMPARISON OF PROPERTIES AND GOLD ADSORPTION WITH DIFFERENT ACTIVATED CARBONS

Activated carbon	Density [kg/m³]	Surface area [m²/g]	Iodine number [mg I₂/g C]	Ash [%]	Gold separation [%]
HSAS C	451.50	1387.30	668.00	0.20	98.15
HSP C	418.50	1101.60	615.00	1.49	80.37
Mooteh C	487.60	1078.00	590.00	2.00	97.69
Gas C	477.00	678.40	617.00	7.76	96.29
CECA C	448.20	1477.70	836.00	8.97	97.92

It was found that the activated carbon produced from apricot stones has the same gold separation efficiency as other imported commercial activated carbons.

Conclusions

Employment of the agricultural by-products as raw materials for the production of activated carbon is a useful recycling process. Considering the large amount of these by-products, their utilization as a source material for activated carbon is expected to provoke a significant economical benefit.

In this work, the production of activated carbon from different agricultural by-products such as bagasse, apricot stones, almond, walnut and hazelnut hard shells has been studied. The activation is performed using phosphoric acid under different operating conditions.

On the basis of obtained experimental results, it can be concluded that these agricultural by–products could react with phosphoric acid to make effective activated carbon. This study shows that feedstock type and activation conditions (such as final activation temperature, activation time and impregnation rate of chemical reagent) are important factors in the quality of activated carbon. High ash content in activated carbons is undesirable because it reduces the mechanical strength and adsorption capacity of activated carbon produced. The ash content can be due to the inorganic constituent of the raw material. The surface area of the obtained activated carbons seems to depend on the ash content, that is, the higher the ash content is, the smaller the surface area is. Thus bagasse has the smallest specific surface area and iodine number. The largest iodine number and surface area were obtained in activated carbon produced from hard shells of apricot stones. The surface area and iodine number of the prepared activated carbon were compared with those of commercial ones.

Our studies suggested that activated carbon from hard shells of apricot stones could be used as an effective adsorbent in the separation of metal ions (such as gold) from wastewaters.

REFERENCES

Ahmenda, M., W.E. Marshall and R.M. Rao "Production of Granular Activated Carbons from Selected Agricultural By-Products And Evaluation of Their Physical, Chemical and Adsorption Properties." Bioresource Technology 71 (2000): 113-23

Aksoylu, A. E., M. Madalena, A. Freitas, M. F. R. Pereira and J. L. Figueiredo; "The Effects of Different Activated Carbon Supports and Support Modifications on the Properties of Pt/AC Catalysts." Carbon 39(2001): 175–85

Aksoylu, A.E., J.L. Faria, M.F.R. Pereira, J.L. Figueiredo, P. Serp, J.-C. Hierso, R. Feurer, Y. Kihn and P. Kalck, "Highly Dispersed Activated Carbon Supported Platinum Catalysts Prepared by OMCVD: A Comparison with Wet Impregnated Catalysts." Applied Catalysis A: General 243 (2003): 357-65.

Arjmand, S., T. Kaghazchi, S. Mehdi Latifi and M. Soleimani; "Chemical Production of Activated Carbon from Nutshells and Date Stones." J. Chem. Eng. Technol., 29 (2006): 986-91.

ASTM International; "Standard Test Method for Determination of Iodine Number of Activated Carbon", Designation D4607-94, West Conshohocken, U.S.A. (2000a) .

ASTM International; "Standard test method for apparent density of activated carbon"; Designation: D 2854-96, West Conshohocken, U.S.A. (2000b).

ASTM International; "Standard Test Method for Total Ash Content of Activated Carbon", Designation D2866-94, West Conshohocken, U.S.A. (2000c).

Bansal, R. C., Goyal, M., "Activated Carbon Adsorption", Taylor & Francis Group; 2005.

Bansode, R. R., J. N. Losso, W. E. Marshall, R. M. Rao and R. J. Portier, "Adsorption of Metal Ions by Pecan Shell-Based Granular Activated Carbon." Bioresour. Technol., 89(2003): 115-19.

Benaddi, H., T. J. Bandosz, J. Jagiello, J. A. Schwarz, J. N. Rouzaud, D. Legras and F. Béguin, "Surface Functionality and Porosity of Activated Carbons Obtained from Chemical Activation of Wood.", Carbon, 38 (2000): 669–74

Brunauer, S., P. H. Emmett and E. Teller; "Adsorption of Gases in Multimolecular layer." J. Am. Chem. Soc., 60(1938): 309-19.

Caglayan, B.S. and A.E. Aksoylu, "CO_2 Adsorption on Chemically Modified Activated Carbon." J. Hazard. Mat. 252-253 (2013): 19-28.

Cox, M. A.A. Pichugin, E.I. El-Shafey and Q. Appleton, "Sorption of Precious Metals onto Chemically Prepared Carbon from Flax Shive." Hydrometallurgy, 78 (2005): 137–44.

Diaz-Teran, J., D. M. Nevskaia, J. L. G. Fierro, A. J. Lopez-Peinado and A. Jerez; "Study of Chemical Activation Process of a Lignocellulosic Material with KOH by XPS and XRD.".Microporous Mesoporous Mater., 60 (2003): 173–81.

Fouladi Tajar, A., T. Kaghazchi and M. Soleimani, "Adsorption of Cadmium from Aqueous Solutions on Sulfurized Activated Carbon Prepared from Nut Shells." J. Hazard. Mat. 165(2009): 1159-64.

Genceli, E., E. Apak, M. Razvigorova, N. Petrov, V. Minkova and E. Ekinci; "Preparation, Modification and Characterization of Pitches from Apricot Stones.". Fuel Process. Technol. 75(2002): 97-107.

Gergova, K. and S. Eser "Effects of activation Method On The Pore Structure of Activated Carbons from Apricot Stones." Carbon 34 (1996): 879-88.

Gonzalez-Serrano, E., T. Cordero, J. Rodriguez-Mirasol and J. Rod-riguez; "Development of Porosity upon Chemical Activation of Kraft Lignin with $ZnCl_2$", Ind. Eng. Chem. Res., 36(1997): 4832–38

Gonzalez, J. F., S. Roman, C. M. Gonzalez-Garcıa, J. M. Valente Nabais and A. Luis Ortiz, "Porosity Development in Activated Carbons Prepared from Walnut Shells by Carbon Dioxide or Steam Activation." Ind. Eng. Chem. Res., 48 (2009): 7474–81.

Hayashi, J., A. Kazehaya, K. Muroyama and A. P. Watkinson; "Preparation of Activated Carbon from Lignin by Chemical Activation.", Carbon, 38 (2000): 1873–78.

Hayashi, J., T. Horikawa, I. Takeda, K. Muroyama and F. Nasir Ani; "Preparing Activated Carbon from Various Nut Shells by Chemical Activation with K_2CO_3.", Carbon, 40(2002a): 2381-86.

Hayashi, J., T. Horikawa, K. Muroyama and V. G. Gomes; "Activated Carbon from Chickpea Husk by Chemical Activation with K_2CO_3: Preparation and Characterization", Microporous Mesoporous Mater., 55(2002b): 63-8.

Johns, M. M., W. E. Marshall and C. A. Toles; "Agricultural By-Products as Granular Activated Carbons for Adsorbing Dissolved Metals and Organics", J. Chem. Technol. Biotechnol., 71(1998): 131-40.

Kaghazchi, T., N. Asasian Kolur and M. Soleimani, "Licorice Residue and Pistachio-Nut Shell Mixture; A Promising Precursor for Activated Carbon." J. Ind. & Eng. Chemistry 16 (2010): 28-37.

Kim, J. W., M. H. Sohn, D. S. Kim, S. M. Sohn and Y. S. Kwon; "Production of Granular Activated Carbon from Waste Walnut Shell and its Adsorption Characteristics for Cu^{2+} Ion", J. Hazard. Mater., 85(2001): 301–15.

Nickolov, R., I. Spassova, N. Velichkova, M. Khristova, V. Dimitrova, P. Tzvetkova "Hybrid Materials as Catalyst Support in NO Reduction with CO." Microporous and Mesoporous Materials 165 (2013): 193-9.

Khristova M. and D. Mehandjiev; "Conversion of NO on a Ni Impregnated-Active Carbon Catalyst in the Presence of Oxygen", Carbon, 36(1998): 1379–85.

Lafi, W.K.; "Production of Activated Carbon from Acorns and Olive Seeds", Biomass Bioenergy, 20(2001): 57-62.

Madadi Yeganeh, M., T. Kaghazchi and M. Soleimani; "Effect of Raw Materials on the Properties of Activated Carbons", J. Chem. Eng. Technol., 29(2006): 1247-51.

Marsh, H., Rodriguez-Reinoso, F. "Activated Carbon", Elsevier; 2006.

Molina-Sabio, M., F. Rodriguez-Reinoso, F. Caturla and M. J. Selles; "Development of Porosity in Combined Phosphoric Acid-Carbon Dioxide Activation." Carbon,

34 (1996): 457-62.

Moreno Castilla, C., F. Carrasco-Marin, M. V. Lopez and M. A. Alvarez-Merino; "Chemical and Physical Activation of Olive-mill Waste water to Produce Activated Carbon", Carbon, 39(2001): 1415-20.

Olivares-Marín, M., C. Fernández-González, A. Macías-García, V. Gómez-Serrano "Preparation of Activated Carbon from Cherry Stones by Physical Activation in Air. Influence of The Chemical Carbonisation with H_2SO_4." J. of Analytical & Applied Pyrolysis 94 (2012) 131-37.

Patric, J.W., Porosity in Carbons, 227-253, Edward Arnold, London, U.K. (1995)

Rubio-Gomez, J., R. M. Martin-Aranda, M. L. Rojas-Cervantes, J. de. D Lopez-Gonzalez. and J. L. G. Fierro; "Ultrasound Enhanced Reactions Involving Activated Carbons as Catalysts: Synthesis of α,β-Unsaturated Nitriles." Carbon, 37(1999): 213–19.

Savova, D., E. Apak, E. Ekinci, F. Yadrim, N. Petrov, T. Budinova, M. Razvigorova and V. Minkova; "Biomass Conversion to Carbon Adsorbents and Gas", Biomass Bioenergy 21(2001): 133-42.

Soleimani, M. and T. Kaghazchi; "Chemical Activation of Agricultural Wastes to Produce Activated Carbon", Proce. of 7th Asia-Pacific International Symposium on combustion and energy utilization, 243-246, Hong Kong P. R. China (2004)

Soleimani, M. and T. Kaghazchi; "The Use of Activated Carbon Prepared from Agriculture Waste in the Separation of Gold from Industrial Wastewaters", Amirkabir J. Sci. and Eng., 15(2005): 139-46.

Soleimani, M. and T. Kaghazchi; "The Investigation of the Potential of Activated Hard Shell of Apricot Stones As Gold Adsorbents." J. Ind. & Eng.Chemistry 14 (2008a): 28-37.

Soleimani, M. and T. Kaghazchi; "Activated Hard Shell of Apricot Stones: A Promising Adsorbent in Gold Recovery." Chinese Journal of Chemical Engineering 16 (2008b): 112-18.

Soleimani, M., "Gold Adsorption from Dilute Solutions with Carbon Adsorbents and Modeling of The Adsorption System", PhD Thesis, Amirkabir University of Technology, 2007

TAPPI standards, "Preparation of Wood for Chemical Analysis T 264 om-88", TAPPI, Norcross, U.S.A. (1988a)

TAPPI standards, "Acid-Insoluble Lignin in Wood and Pulp T 222 om-88", TAPPI, Norcross, U.S.A. (1988b)

TAPPI standards; "Ash in Wood, Pulp, Paper and Paperboard: Combustion at 525°C T211 om-93", TAPPI, Norcross, U.S.A. (1993)

Toles, C.A., W. E. Marshall, M. M. Johns, L.H. Wartelle and A. McAloon; "Acid-Activated Carbons from Almond Shells: Physical, Chemical and Adsorptive Properties and Estimated Cost of Production", Bioresour. Technol., 71(2000): 87-92.

Tongpoothorn, W., Sriuttha, M., Homchan, P., Chanthai, S., and C. Ruangviriyachai, "Preparation of Activated Carbon Derived from Jatropha Curcas Fruit Shell by Simple Thermo-Chemical Activation and Characterization of Their Physico-Chemical Properties." Chem. Eng. Res. Des. 89 (2011); :335–340

Yang, T. and A. C. Lua; "Characteristics of Activated Carbons Prepared from Pistachio-Nut Shells by Potassium Hydroxide Activation", Microporpos Mesoporous Mater., 63(2003): 113-24.